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NEW PATENT APPLICATION

ATOMIC LAYER DEPOSITION PROCESS AND APPARATUS

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ATOMIC LAYER DEPOSITION PROCESS AND APPARATUS

Background of the Invention

[0001] This invention is directed to atomic layer deposition. More particularly this invention provides an apparatus and process in which precursor gas is delivered to a process reactor chamber at reduced pressure from an auxiliary chamber through a pressure equalization process. The precursor gas flows into the reactor chamber from the auxiliary chamber solely due to a pressure gradient between the two chambers thereby reducing use of excess precursor gas and ensuring spatial uniformity of layers produced in the atomic layer deposition process.

[0002] Atomic layer deposition is a method of depositing very thin films onto a surface. Individual precursor gases are pulsed onto the surface, typically a wafer, in a sequential manner without mixing the precursors in the gas phase. Each precursor gas reacts with the surface to form an atomic layer in a way such that only one layer at a time can be deposited onto the surface.

[0003] Preferably, each of the precursor gases reacts with each other only at surfaces where they are deliberately deposited. To avoid direct contact between the different precursor gases, introduction of precursor gases to the process reactor chamber is often interleaved with a flow of purge gas.

[0004] There are several drawbacks to current procedures for introducing precursor gas to the process reactor chamber. The thickness of the layer of precursor adsorbed onto the target surface depends upon the gas impingement rate on the target surface, and thus the local

pressure. When precursor gas is delivered over a flow line, the pressure varies over the flow line and consequently, the gas will not be adsorbed uniformly over the target surface. Second, the major portion of the precursor gas delivered is not used to form the monolayer, but flowed through the system and thus wasted. The relatively slow time response of mass flow controllers using to meter the precursor gas into the process reactor chamber is a contributing factor to the inefficiency of gas usage. In fact, after mass flow controllers are set to deliver a predetermined flow to a process reactor chamber as part of the atomic layer process, the flow is often kept constant and merely switched between the process reactor chamber and a disposal pump. In addition to the enormous waste of precursor gas, this procedure results in pumping problems due to volume reactions in the foreline, the pumps and the abatement system.

Summary of the Invention

[0005] It is an object of the invention to provide an atomic layer deposition arrangement and process which avoids undesirable condensation of precursor gases.

[0006] Another object of the invention is to provide an atomic layer deposition arrangement and process which minimizes waste of precursor gases.

[0007] A further object of the invention is to provide an atomic layer deposition arrangement and process which promotes spatial uniformity of the thickness of adsorption layers.

[0008] These and other objects of the invention are achieved by providing an atomic layer deposition arrangement comprising a process reactor chamber having at least one inlet and at least one outlet, a first auxiliary chamber for receiving a first precursor gas coupled to the process reactor chamber, a first precursor gas supply coupled to the first auxiliary chamber through a first flow path, at least one precursor gas valve in the first flow path between an inlet of the process reactor chamber and the auxiliary chamber, a second auxiliary chamber for receiving a second precursor gas coupled to the process reactor chamber through a second flow path, at least one second precursor gas valve in the second flow path between an inlet of the process reactor chamber and the second auxiliary chamber, a second precursor gas supply coupled to the second auxiliary chamber, and an exhaust pump coupled to the at least one outlet of the process reactor chamber, wherein the first flow path and second flow path does not include a mass flow controller.

[0009] The invention also provides a method of delivering precursor gas to an atomic layer deposition chamber comprising closing a first precursor gas valve located in between a first auxiliary chamber and an inlet of a process reactor chamber, closing a second precursor gas valve located in between a second auxiliary chamber and an inlet of the process reactor chamber, reducing pressure in the process reactor chamber, opening the first precursor gas valve, allowing a first precursor gas to flow from the first auxiliary chamber to the process reactor chamber solely under a pressure gradient, closing the first precursor gas valve, reducing pressure in the process reactor chamber, opening the second precursor gas valve, and allowing a second precursor gas to flow from the second auxiliary chamber to an inlet of the process reactor chamber solely under a pressure gradient.

Brief Description of the Drawings

[00010] Figure 1(a)-1(e) are schematic representations of a method and arrangement for delivery of a first precursor gas in accordance with the invention;

[00011] Figure 2(a)-2(e) are schematic representations of a method and arrangement for delivery of a second precursor gas in accordance with the invention;

[00012] Figure 3 is an illustration of an atomic layer deposition arrangement in accordance with the invention; and

[00013] Figure 4 is an illustration of an atomic layer deposition arrangement including a purge gas in accordance with the invention.

Detailed Description of the Preferred Embodiments

[00014] An atomic layer deposition arrangement in accordance with the invention is shown in Figure 1(a). A process reactor chamber 10 is coupled to an exhaust pump (not shown) via a vacuum valve 12 coupled to an outlet 14 of the process reactor chamber 10. The process reactor chamber 10 is also coupled through inlets 16 and 18 to a first auxiliary chamber 20 having a volume V_1 containing a first precursor gas and a second auxiliary chamber 22 having a volume V_2 containing a second precursor gas. Gas valves 24 and 26 are located in between the first auxiliary chamber 20 and process reactor chamber inlet 16, and in between the second auxiliary chamber 22 and process reactor chamber inlet 18, respectively.

[00015] In one embodiment of the method according to the invention, the pressure in process reactor chamber 10 is reduced by opening valve 12 coupled to an exhaust pump with valves 24 and 26 in a closed position as shown in Fig. 1(a). Next, as shown in Fig. 1(b) valve 24 is opened and the first precursor gas discharges from first auxiliary chamber 20 into process reactor chamber 10 due to the pressure gradient between first auxiliary chamber 20 and process reactor chamber 10. The first precursor gas will apportion itself between process reactor chamber 10 and first auxiliary chamber 20 according to chamber volumes, approximately in accordance with the following equation,

$$P_1 V_1 = Pr_1 (V_1 + Vr)$$

[00016] where Vr is the process reactor chamber volume, P_1 is the pressure in the first auxiliary chamber before discharge and Pr_1 is the pressure in the first auxiliary chamber and process reactor chamber after discharge.

[00017] Apportionment of the first precursor gas between first auxiliary chamber 20 and process reactor chamber 10 is illustrated in Fig. 1(b). After discharge of the first precursor gas into the process reactor chamber 10, valve 24 is closed as illustrated in Fig. 1(c). Valve 12 is then opened and pressure reduced in process reactor 10 as shown in Fig. 1(d). After a reduced pressure is achieved in process reactor 10, valve 12 is closed as shown in Fig. 1(e) and Fig. 2(a).

[00018] Next, as shown in Fig. 2(b), valve 26 is opened and the second precursor gas discharges from the second auxiliary chamber 22 into process reactor chamber 10 due to the pressure gradient between the second auxiliary chamber 22 and process reactor chamber 10.

The second precursor gas will apportion itself between process reactor 10 and second auxiliary chamber 22 according to chamber volume, approximately in accordance with the following equation

$$P_2 V_2 = Pr_2 (V_2 + Vr)$$

[00019] Where P_2 is the pressure in auxiliary chamber 22 before discharge and Pr_2 is the pressure in the second auxiliary chamber and process reactor chamber after discharge. After discharge of the second precursor gas into the process reactor chamber 10, valve 26 is closed as illustrated in Fig. 2(c). Valve 12 is then opened and pressure reduced in process reactor chamber 10 as shown in Fig. 2(d). After a reduced pressure is achieved in process reactor 10, valve 12 is closed as shown in Fig. 2(e).

[00020] The above is repeated, alternating gas discharge from first auxiliary chamber 20 and second auxiliary chamber 22 until the desired thickness of deposition layer is obtained.

[00021] The first auxiliary chamber 20 and second auxiliary chamber 22 may be coupled by an intermittent valve connection to any suitable gas supply and recharged in between alternating discharge of the first precursor gas and second precursor gas to the process reactor chamber.

[00022] As is well known by those of skill in the art, the gas supply source can be a pressurized gas source such as a gas cylinder or a chamber including a solid or liquid substance. The chamber is heated to vaporize the substance and obtain a desired vapor pressure. The first auxiliary chamber 20 and second auxiliary chamber 22 may itself contain a

solid or liquid substance and be heated to a predetermined temperature to vaporize the substance and obtain the desired vapor pressure.

[00023] Optionally, process reactor chamber 10 may be purged with an inert gas after evacuation as in Fig. 1(d) or Fig. 2(d) and prior to introduction of an alternate precursor gas as in Fig. 1(b) of Fig. 2(b).

[00024] Precursors for use in ALD are well known to those skilled in the art. Examples of commonly used precursors include $Zr(OC_4H_9)_4$ and O_2, $ZrCl_4$ and H_2O, $HfCl_4$ and H_2O, 2,2,6,6-tetramethyl-3,5-heptanedionato Yttrium ("$Y(thd)_3$") and O_3, $Al(CH_3)_3$ and H_2O, $Al(CH_3)_3$ and O_2, dimethylaluminumhydride ethylene-piperidine-pyrocatechol ("DMAH-EPP") and NH_3, tetrakis dimethylamino titanium ("TDMAT") and NH_3, $TiCl_4$ and NH_3, $TiCl_4$ and H_2/N_2, $TiCl_4$ and H_2, $TiCl_4$ and H_2O, $TiCl_4$ and O_2, $Ti(OCH(CH_3)_2))_4$ and O_2, $TaCl_5$ and NH_3, $Ta(OC_2H_5)_5$ and H_2O, strontiumbis (triisopropylcyclopentadienyl) ("$Sr(C_5iPr_3H_2)_2$ ")and O_2, $Zn(CH_2CH_3)_2$ and H_2O, and tetrakis (organo-amino) hafnium compounds, for example tetrakis (dimethylamino) hafnium, tetrakis (diethylamino) hafnium, tetrakis (ethylmethylamino) hafnium and H_2O.

[00025] The invention will be further described by the following examples which are illustrative only and do not limit the invention.

[00026] Figure 3 illustrates an embodiment for the manufacture of thin films according to the present invention. In the interior of a process reactor chamber 10 is a substrate holder 30 which can be heated by electrical power to a predetermined temperature. This temperature is referred to as the deposition temperature. A substrate 32 is mounted on the

substrate holder such that good thermal contact is established between substrate holder 30 and substrate 32. By conducting the process according to this invention, thin films are deposited at the exposed surface of substrate 32. The process reactor chamber 10 is made of stainless steel and is vacuum-pumped by a vacuum pumping system (not shown). The vacuum system pumping system is connected to the process reactor chamber 10 by means of a high conductance vacuum valve 12. Vacuum valve 12 is either in an open or closed position, transitioning between these states with a fast acting mechanism. The connecting vacuum valve is manufactured by BOC Edwards, model number QVA060. The interior of the process reactor chamber 10 is pumped down to a base pressure of 10^{-5} Torr by the evacuation system when vacuum valve 12 is in its open position. The pressure of process reactor chamber 10 is typically less than 10^{-3} Torr 10 minutes after vacuum valve 12 has been closed, indicating leak tightness of the vessel. In normal operation, there is no provision to either measure or control the pressure of process reactor chamber 10.

[00027] The process reactor chamber 10 is connected to a source-material delivery system consisting of two vessels 20 and 22 connected by gas valves 24 and 26 respectively, to the process reactor chamber 10. Vessels 20 and 22 are made of stainless steel. Vessel 20 and its connecting valve 24 can be electrically heated to temperatures up to 300° C. The connecting high temperature valve is provided by Fujikin, model number FWBR-71-9.52. Vessels 20 and 22 are connected via valves 34 and 36, respectively to sources of material at constant pressure. In the case that two gases are used, these sources are usually gas cylinders with regulators to ensure a constant delivery pressure. In the case, one of the sources is liquid or solid at room temperature, precursor material is preloaded into vessel 20 through either valve 34 or through a fill opening in the wall of vessel 20 which can be closed gas tight.

[00028] For the apparatus and method shown in Figure 3 and by way of example, the net volume enclosed between valves 24, 26 and 12 is 378 cc. Low vapor pressure materials, either liquids or solids are loaded in vessel 20. This vessel and valve 24 are heated to a predetermined temperature referred to as the vaporization temperature. The net volume of vessel 20 is 231 cc and the volume of vessel 22 is 37 cc.

[00029] All the valves in the system are opened and closed at pre-programmed times by a system controller, typically a computer, a programmable logic controller (PLC) or a microprocessor.

Example 1

[00030] For deposition of titanium nitride films, one of the source materials used is titaniumtetrachloride while the second gas is ammonia gas. Thirty cc of titaniumtetrachloride is loaded at room temperature as a liquid into vessel 20. The ammonia gas is supplied to vessel 22 from a gas cylinder with a regulator set at 30 psi (gauge pressure). The deposition process is started by affixing a silicon wafer which is the substrate 32, to the substrate holder 30, then closing valves 24 and 26 and opening the vacuum valve 12, thus evacuating the process reactor chamber. The substrate holder 30 and, by inference the substrate 32, is heated to the deposition temperature of 400° C. The vessel 20 containing titaniumtetrachloride and its connecting valve 24 are heated to a vaporization temperature of about 60° C. Valve 26 is briefly opened to evacuate vessel 22 and closed. When valve 26 has reached closure, valve 36 is opened for a time long enough for vessel 22 to be charged with ammonia gas at a pressure of 30 psi. In this system, valve 26 is kept open for 2 seconds. Valve 36 is opened and closed at regular intervals to keep the vessel 22 charged at 30 psi.

[00031] Once the pressure in vessel 20 reaches 60 Torr, valve 12 is closed and when it reaches closure valve 24 is opened, kept open for 1 second and then closed. From previous diagnostic pressure measurements, it is known that the process vessel is now filled with titaniumtetrachloride at a pressure between 10 and 20 Torr. One second after valve 24 reaches closure, valve 12 is opened for 15 seconds and then closed. From previous measurements it is known that the pressure of titanium chloride in the process vessel is now less than 10^{-4} Torr. At the moment that valve 12 reaches closure, valve 26 is opened for 1 second. From previous diagnostic pressure measurements it is known that ammonia is now present in the process vessel at a pressure of 20 Torr. One second after valve 26 reaches closure, valve 12 is opened for 15 seconds and then closed. From previous measurements it is known that the pressure of ammonia in the process vessel is now less than 10^{-4} Torr.

[00032] This sequence has exposed the surface of the silicon wafer 32 to titaniumtetrachloride and to ammonia, respectively, under isobaric conditions. This complete cycle is referred to as one deposition cycle. In this deposition cycle a monolayer of a film which is substantially titanium nitride is uniformly deposited on the surface of the silicon wafer 32. A desired film thickness is obtained by repeating the deposition cycle a sufficient number of times. After 50 deposition cycles all valves are closed, the substrate temperature is allowed to decrease to room temperature and the process reactor chamber 10 is vented to atmospheric pressure. The silicon wafer substrate with the titanium nitride film is removed from the system and the deposited film is measured for thickness uniformity across the wafer surface. The thickness uniformity is found to be better than the measurement error of the measurement apparatus and the non-uniformity is estimated to be less than 1%.

Example 2

[00033] In a further embodiment shown in Figure 4, a third vessel 38, with internal volume of 73 cc but otherwise identical to the vessels 20 and 22 is charged with 150 psi (gauge pressure) of argon. This vessel is discharged to process reactor chamber 10 right after valve 12 is opened to drive the titaniumtetrachloride and then the ammonia out of the system and decrease the pumping time to 5 seconds instead of 15 seconds in both cases.

[00034] As mentioned above, the invention has the desirable effect of improving the thickness uniformity of a film deposited by means of an atomic layer deposition method whereby the gases are in contact with the substrate surface under conditions of zero flow. Another advantage of this invention is the simplicity of the apparatus because the process obviates the need for complicated measurements of flow and pressure.

[00035] The atomic layer deposition arrangement and process of the invention minimizes waste of precursor gases, decreases process costs and minimizes problems associated with delivery of precursor gas to the process reactor chamber by pumping. The adsorption of precursor gas by a substrate in a process without gas flow by pumping ensures the spatial uniformity of the layer deposited on the substrate.

[00036] Although preferred embodiments are specifically illustrated and described herein above, it will be appreciated that many modifications and variations of the present invention are possible in light of the above teachings and within the purview of the appended claims without departing from the spirit and intended scope of the invention.